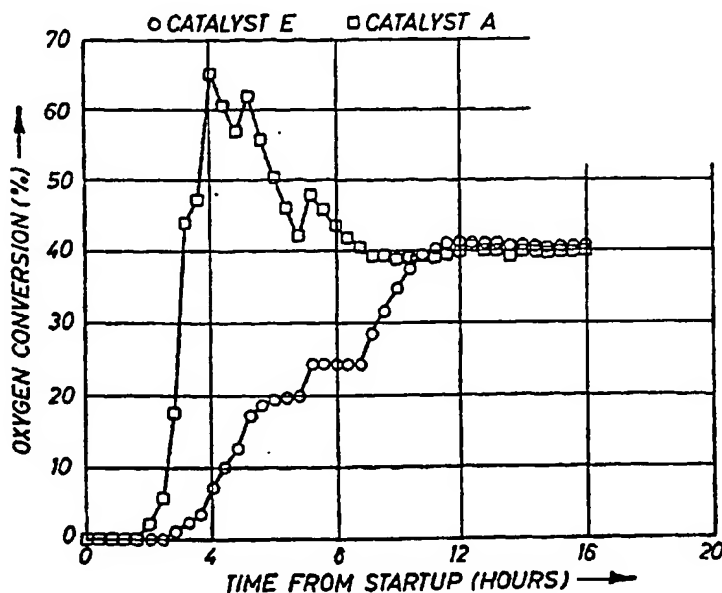




## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>6</sup> : <b>B01J 23/66, C07D 301/10</b>		A1	(11) International Publication Number: <b>WO 95/05896</b>
			(43) International Publication Date: <b>2 March 1995 (02.03.95)</b>
(21) International Application Number: <b>PCT/EP94/02783</b>		(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, ES, FI, GB, GE, HU, JP, KE, KG, KP, KR, KZ, LK, LT, LU, LV, MD, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SI, SK, TJ, TT, UA, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD).	
(22) International Filing Date: <b>22 August 1994 (22.08.94)</b>			
(30) Priority Data: <b>08/110,282      23 August 1993 (23.08.93)      US</b>			
(71) Applicant: <b>SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V. [NL/NL]; Carel van Bylandtlaan 30, NL-2596 HR The Hague (NL).</b>		Published <i>With international search report.</i>	
(72) Inventor: <b>MATUSZ, Marek; 14515 Meeting Lane, Houston, TX 77084 (US).</b>			

(54) Title: ETHYLENE OXIDE CATALYST



## (57) Abstract

This invention relates to an ethylene oxide catalyst which contains, prior to the catalyst's first use in the conversion of ethylene to ethylene oxide, silver, one or more alkali metal promoters and  $0.4 \times 10^{-3}$  to  $4.0 \times 10^{-3}$  moles of chloride per mole of silver deposited on an alpha alumina carrier. The catalyst provides for an improved start-up when started up in the presence of ethylene oxide, oxygen and chlorohydrocarbon moderator.

BEST AVAILABLE COPY

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LJ	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

- 1 -

## ETHYLENE OXIDE CATALYST

The invention relates to silver-containing catalysts suitable for the preparation of ethylene oxide.

Catalysts for the production of ethylene oxide from ethylene and molecular oxygen are generally supported silver catalysts. Such catalysts are typically promoted with alkali metals. The use of small amounts of the alkali metals potassium, rubidium and cesium were noted as useful promoters in supported silver catalysts in U.S. Patent No. 3,962,136, issued June 8, 1976, and U.S. Patent No. 4,010,115, issued March 1, 1977. The use of other co-promoters, such as rhenium, or rhenium along with sulphur, molybdenum, tungsten and chromium is disclosed in U.S. Patent No. 4,766,105, issued August 23, 1988, and U.S. Patent No. 4,808,738, issued February 28, 1989. U.S. Patent No. 4,908,343, issued March 13, 1990, discloses a supported silver catalyst containing a mixture of a cesium salt and one or more alkali metal and alkaline earth metal salts.

The use of chloride moderators to enhance the yield of silver-based ethylene oxide catalysts is known in the art. The chloride is provided as chlorohydrocarbon moderators in the reaction gases or as chloride anions incorporated into the catalyst during the catalyst preparation phase. Earlier practice tended to emphasize the latter practice whereas more recent practice tends to emphasize the former practice. The use of chloride-containing compounds to prepare catalysts can be found in U.S. Patent Numbers 2,615,900, issued October 28, 1952; 2,709,173, issued May 24, 1955; 2,765,283, issued October 2, 1956; 2,769,016, issued October 30, 1956; 2,799,687, issued July 16, 1957; 3,585,217, issued June 15 1971; 4,415,476, issued November 15, 1983; and 4,904,343, issued March 13, 1990.

During the initial phase of catalyst start-up of the alkali metal doped silver-based catalysts in commercial ethylene oxide reactors even in the presence of chlorohydrocarbon moderators the

- 2 -

catalysts experience the so-called breakthrough phase, during which the oxygen conversion is very high and the selectivity is very low. The reaction is difficult to control at this stage. It might take days in a commercial start-up for the conversion to drop so that the reaction can be controlled. Substantial economic incentive exists to shorten the start-up period and make the catalysts operate at higher selectivities since the selectivity determines the yield of ethylene oxide product.

In U.S. patent numbers 5,155,242, issued October 13, 1992, and 4,874,879, issued October 17, 1989, there is disclosed an improved start-up procedure wherein the catalysts are subjected to a pres soak period in the presence of a chlorohydrocarbon moderator at a temperature less than the operating temperature of the reactor. While this technique does improve catalyst start-up, it can be subject to operator error. Over- and under-moderating with the chlorohydrocarbon moderator during the presoak can adversely affect start-up and post start-up operations. It would be desirable to have a catalyst that could be loaded into a reactor and started up in the presence of a chlorohydrocarbon moderator without any special pre-chloriding procedures needing to be applied to the catalyst in the reactor.

The invention relates to a catalyst suitable for the production of ethylene oxide catalyst from ethylene and molecular oxygen in the vapour phase which catalyst comprises a catalytically effective amount of silver, a promoting amount of alkali metal and, prior to the catalyst's first use in producing ethylene oxide, from  $0.4 \times 10^{-3}$  to  $4 \times 10^{-3}$  moles of chloride per mole of silver supported on a carrier comprising at least 85 percent by weight of alpha alumina.

It has been found that catalysts containing a selected amount of chloride have improved start-up characteristics over catalysts without such chloride when such catalysts are started up in the presence of ethylene, oxygen and a chlorohydrocarbon moderator. The presence of the chloride allows the catalyst to reach higher selectivity levels earlier than catalysts without such chloride.

- 3 -

Thus, an improved process for starting up a fixed bed ethylene oxide reactor containing fresh or unused catalyst is obtained.

Figure 1 is a plot of the selectivity of ethylene to ethylene oxide as a function of time for a Comparative Catalyst A and two catalysts of this invention (B and C) during the start-up of an ethylene oxide reactor.

Figure 2 is a plot of the oxygen conversion as a function of time for a Comparative Catalyst A and two catalysts of this invention (B and C) during the start-up of an ethylene oxide reactor.

Figure 3 is a plot of the selectivity of ethylene to ethylene oxide as a function of time for a Comparative Catalyst A and a catalyst of this invention (E) during the start-up of an ethylene oxide reactor.

Figure 4 is a plot of the oxygen conversion as a function of time for a Comparative Catalyst A and a catalyst of this invention (E) during the start-up of an ethylene oxide reactor.

The catalysts of the instant invention comprise a catalytically effective amount of silver, a promoting amount of alkali metal and, prior to the catalyst's first use in producing ethylene oxide, from  $0.4 \times 10^{-3}$  to  $4 \times 10^{-3}$  moles of chloride per mole of silver supported on an alpha alumina support. Other promoters in promoting amounts may be optionally present such as rare earths, magnesium, rhenium and rhenium co-promoters selected from sulphur, chromium, molybdenum, tungsten and mixtures thereof.

In general, the catalysts of the present invention are prepared by impregnating porous refractory supports comprising alpha alumina with silver ions or compound(s), complex(es) and/or salt(s) dissolved in a suitable solvent sufficient to cause deposition on the support of from 1 to 40, preferably from 1 to 30 percent by weight, basis the weight of the total catalyst, of silver. The impregnated support is then separated from the solution and the deposited silver compound is reduced to metallic silver. Also deposited on the support either prior to, coincidentally with, or

- 4 -

subsequent to the deposition of the silver will be suitable ions, or compound(s) and/or salt(s) of alkali metal dissolved in a suitable solvent. Also deposited on the carrier coincidentally with the deposition of the silver and/or alkali metal will be suitable optional promoter compound(s), complex(es) and/or salt(s) dissolved in an appropriate solvent. Also deposited on the support either prior to, coincidentally with, or subsequent to the deposition of the silver and/or alkali metal and/or optional promoters will be chlorine in the form of chloride ( $\text{Cl}^{-1}$ ) dissolved in an appropriate solvent.

The carrier or support employed in these catalysts in its broadest aspects can be any of the large number of conventional, porous refractory catalyst carriers or support materials which are considered relatively inert in the presence of ethylene oxidation feeds, products and reaction conditions. Such conventional materials are known to those skilled in the art and may be of natural or synthetic origin and preferably are of a macroporous structure, i.e., a structure having a surface area below  $10 \text{ m}^2/\text{g}$  and preferably below  $3 \text{ m}^2/\text{g}$ . Particularly suitable supports are those of aluminous composition. Preferred supports comprise the aluminous materials, in particular those comprising alpha alumina. In the case of alpha alumina-containing supports, preference is given to those having a specific surface area as measured by the B.E.T. method of from  $0.03 \text{ m}^2/\text{g}$  to  $10 \text{ m}^2/\text{g}$ , preferably from  $0.05 \text{ m}^2/\text{g}$  to  $5 \text{ m}^2/\text{g}$ , more preferably from  $0.1 \text{ m}^2/\text{g}$  to  $3 \text{ m}^2/\text{g}$ , and a water pore volume as measured by conventional water absorption techniques of from 0.1 to 0.75 ml/g by volume. The B.E.T. method for determining specific surface area is described in detail in Brunauer, S., Emmet, P. Y. and Teller, E., J. Am. Chem. Soc., 60, 309-16 (1938).

Certain types of alpha alumina containing supports are particularly preferred. These alpha alumina supports have relatively uniform pore diameters and are more fully characterized by having B.E.T. specific surface areas of from  $0.1 \text{ m}^2/\text{g}$  to  $3 \text{ m}^2/\text{g}$ , preferably from  $0.1 \text{ m}^2/\text{g}$  to  $2 \text{ m}^2/\text{g}$ , and water pore volumes of from

- 5 -

0.10 ml/g to 0.55 ml/g. Typical properties of some supports found particularly useful in the present invention are presented in Table I. Suitable manufacturers of carriers comparable to those in Table I include Norton Company and United Catalysts, Inc. (UCI).

TABLE I

Carrier	A	B	C	D	E	F
B.E.T. Surface Area, m <sup>2</sup> /g (a)	0.21	0.42	0.51	0.48	0.57	2.06
Water Pore Volume, ml/g	0.26	0.36	0.38	0.46	0.44	0.65
Crush Strength, FPCS, kg (b)	20	15	21	17	15	No Data
Total Pore Volume, Hg, ml/g (c)	1.26	0.42	0.40	0.46	0.42	0.65
Average Pore Diameter, Hg, nm (c)	6200	5600			7700	10000
Median Pore Diameter, Hg, μ (c,e)	3.7	2.7	3.5	6.2	2.4	2.5
Percent Pore Volume in Pores Greater Than 35 nm (c)	90.0%	88.5%	93.0%		91.5%	94.1%
Percent Pore Volume in Pores Greater Than 1 μm (c)	87.0%	82.5%	77.0%		83.5%	61.0%
% Wt. Alpha Alumina	99.5	98	98.8	99.2	98	70-75
Water Leachable Na, ppmw	12	53	16	16	18	No Data
Acid-Leachable Na, ppmw	40	96	188	42	45	No Data
Water Leachable K, ppmw	5	22	32	38	10	No Data
Acid-Leachable Fe, ppmw	2	5	No Data	1	5	No Data
% Wt. SiO <sub>2</sub>	.5	2	0.1	0.8	2	25-30

(a) Method of Brunauer, Emmet and Teller, loc. cit.

(b) Flat Plate Crush Strength, single pellet.

(c) Determined by mercury intrusion to 380,000 kPa using Micromeritics Autopore

9200 or 9210 (130° Contact angle, 0.473 N/m surface tension of Hg).

(e) Median pore diameter represents the pore diameter wherein 50% of the total pore volume is found in pores having less than (or greater than) the median pore diameter.



- 7 -

Of the carriers listed in TABLE I D is a preferred carrier. Other desirable supports are those such as described in U.S. patent No. 5,145,824.

5 The support, irrespective of the character of the support or carrier used, is preferably shaped into particles, chunks, pieces, pellets, rings, spheres, wagon wheels, and the like of a size suitable for use in fixed bed reactors. Conventional commercial fixed bed reactors are typically in the form of a plurality of parallel elongated tubes (in a suitable shell) approximately 18 to 10 69 mm O.D. and 12 to 25 mm I.D. and 4.5-14 m long filled with catalyst. In such reactors, it is desirable to use a support formed into a rounded shape, such as, for example, spheres, pellets, rings, tablets and the like, having diameters from about 2.5 to 20 mm.

15 Particular supports having differing properties such as surface area and pore volume may be selected in order to provide particular catalytic properties. With regard to surface area (B.E.T.), a possible lower limit is  $0.01 \text{ m}^2/\text{g}$  and a possible upper limit is  $10 \text{ m}^2/\text{g}$ . With regard to water pore volume, a possible lower limit is  $0.05 \text{ ml/g}$  and a possible upper limit is  $0.8 \text{ ml/g}$ .

20 The catalysts of the present invention are prepared by a technique in which the alkali metal promoters and the chloride in the form of soluble salts and/or compounds are deposited on the catalyst and/or support prior to, simultaneously with, or subsequent to the deposition of the silver and each other. The preferred 25 method is to deposit silver, alkali metal and chloride simultaneously on the support, that is, in a single impregnation step, although it is believed that the individual or concurrent deposition of the alkali metal and chloride prior to and/or subsequent to the deposition of the silver would also produce 30 suitable catalysts.

Promoting amounts of alkali metal or mixtures of alkali metal are deposited on a porous support using a suitable solution. Although alkali metals exist in a pure metallic state, they are not suitable for use in that form. They are used as ions or compounds

- 8 -

of alkali metals dissolved in a suitable solvent for impregnation purposes. The carrier is impregnated with a solution of alkali metal promoter ions, salt(s) and/or compound(s) before, during or after impregnation of the silver ions or salt(s), complex(es), and/or compound(s) has taken place. An alkali metal promoter may even be deposited on the carrier after reduction to metallic silver has taken place. The promoting amount of alkali metal utilized will depend on several variables, such as, for example, the surface area and pore structure and surface chemical properties of the carrier used, the silver content of the catalyst and the particular ions used in conjunction with the alkali metal cation, optional co-promoters. The amount of alkali metal promoter deposited upon the support or present on the catalyst generally lies between about 10 parts per million and about 3000 parts per million, preferably between about 15 parts per million and about 2000 parts per million and more preferably, between about 20 parts per million and about 1500 parts per million by weight of total catalyst. Most preferably, the amount ranges between about 50 parts per million and about 1000 parts per million by weight of the total catalyst. The degree of benefit obtained within the above-defined limits will vary depending upon particular properties and characteristics, such as, for example, reaction conditions, catalyst preparative techniques, surface area and pore structure and surface chemical properties of the carrier utilized, silver content of the catalyst, and other compounds, cations or anions present in addition to alkali metal ions, and the above-defined limits were selected to cover the widest possible variations in properties and characteristics. The effects of these variation in properties are readily determined by experimentation. The alkali metal promoters are present on the catalysts in the form of cations (ions) or compounds of complexes or surface compounds or surface complexes rather than as the extremely active free alkali metals, although for convenience purposes in this specification and claims they are referred to as "alkali metal" or "alkali metal promoters" even though they are not present on the

- 9 -

catalyst as metallic elements. For purposes of convenience, the amount of alkali metal deposited on the support or present on the catalyst is expressed as the metal. Without intending to limit the scope of the invention, it is believed that the alkali metal compounds are oxidic compounds. More particularly, it is believed that the alkali metal compounds are probably in the form of mixed surface oxides or double surface oxides or complex surface oxides with the aluminium of the support and/or the silver of the catalyst, possibly in combination with species contained in or formed from the reaction mixture, such as, for example, chlorides or carbonates or residual species from the impregnating solution(s).

In a preferred embodiment, at least a major proportion (greater than 50%) of the alkali metals are selected from the group consisting of potassium, rubidium, cesium, and mixtures thereof. As used herein, the term "alkali metal" and cognates thereof refers to the alkali metals selected from the group consisting of lithium, sodium, potassium, rubidium, cesium and mixtures thereof. As used herein, the term "mixtures of alkali metals" or cognates of these terms refers to the use of two or more of the alkali metals, as appropriate, to provide a promoting effect. Non-limiting examples include cesium plus rubidium, cesium plus potassium, cesium plus sodium, cesium plus lithium, cesium plus rubidium plus sodium, cesium plus potassium plus sodium, cesium plus lithium plus sodium, cesium plus rubidium plus potassium plus sodium, cesium plus rubidium plus potassium plus lithium, cesium plus potassium plus lithium and the like. A preferred alkali metal promoter is cesium. A particularly preferred alkali metal promoter is cesium plus at least one additional alkali metal. The additional alkali metal is preferably selected from sodium, lithium and mixtures thereof, with lithium being preferred.

It should be understood that the amounts of alkali metal promoters on the catalysts are not necessarily the total amounts of these metals present in the catalyst. Rather, they are the amounts of alkali metal promoters which have been added to the catalyst by

- 10 -

impregnation with a suitable solution of ions, salts and/or compounds and/or complexes of alkali metals. These amounts do not include amounts of alkali metals which are locked into the support, for example, by calcining, or are not extractable in a suitable solvent such as water or lower alkanol or amine or mixtures thereof and do not provide a promoting effect. It is also understood that a source of the alkali metal promoter ions, salts and/or compounds used to promote the catalyst may be the carrier. That is, the carrier may contain extractable amounts of alkali metal that can be extracted with a suitable solvent, such as water or lower alkanol, thus preparing an impregnating solution from which the alkali metal ions, salts and/or compounds are deposited or redeposited on the support.

Other promoters and copromoters can be used in conjunction with the silver and alkali metal promoters. Non-limiting examples of other promoters include rhenium, sulphur, molybdenum, tungsten and chromium (see U.S. patent no. 4,766,105, issued August 23, 1988); sulfate anion, fluoride anion, oxyanions of Groups 3b to 6b (see U.S. patent no. 5,102,848, issued April 7, 1992); (i) oxyanions of an element selected from Groups 3 through 7b and (ii) alkali(ne) metal salts with anions of halides, and oxyanions selected from Groups 3a to 7a and 3b through 7b (see U.S. patent no. 4,908,343, issued March 13, 1990).

Moderating amounts of chloride are deposited on a porous support using a suitable impregnating solution. It is understood that chloride when deposited on the support will be present in the anionic state, i.e., as  $\text{Cl}^{-1}$ , and that there will also be present on the support a balancing cation. The exact form of this balancing cation is not known, although it is speculated that will be one of the promoter cations or silver or both. The chloride is deposited as ions, salts or compounds dissolved in a suitable solvent for impregnation purposes. The carrier is impregnated with a solution of the chloride moderator ions, salt(s) and/or compound(s) before, during or after impregnation of the silver ions or salt(s),

- 11 -

complex(es), and/or compound(s) has taken place and before, during or after impregnation of the promoter ions or salt(s), complex(es), and/or compound(s) has taken place. The chloride moderator may even be deposited on the carrier after reduction to metallic silver has taken place. Suitable chloride-containing salts used to prepare the impregnating solutions include promoter chlorides such as lithium chloride, sodium chloride, potassium chloride, rubidium chloride and cesium chloride as well as ammonium chloride. Ammonium chloride is a preferred salt for use in preparing the chloride-containing impregnating solutions. Other compounds which decompose to the chloride ion upon processing of the catalyst are also suitable. The chloride-containing impregnating solutions will normally contain at least a small amount of water to enhance solubility of the chloride-containing salt or compound.

The amount of chloride deposited upon the support or present on the catalyst is a function of the amount of silver present on the catalyst and generally ranges from about  $0.4 \times 10^{-3}$  to about  $4 \times 10^{-3}$  moles of chloride per mole of silver. Lesser amounts do not provide a moderating effect and greater amounts adversely effect activity and selectivity. In a preferred embodiment where the catalyst contains from about 12 to about 18 weight percent of silver, the chloride content will range from about 20 parts per million to about 200 parts per million by weight of the total catalyst.

The term "moderating" as used herein with reference to the chloride deposited on the fresh or unused catalyst refers to a change in the catalyst properties that allows the catalyst during start-up to obtain higher selectivities in a shorter period of time than does a catalyst that has not been moderated. It is also understood that the moderating amounts of chloride deposited on the support are those amounts that are applied to a fresh or unused catalyst by an impregnation step. During use a silver-based ethylene oxide catalyst will obtain a certain amount of chloride deposited thereon because the catalyst is operated in an environment containing small amounts of chlorohydrocarbons, but this latter

- 12 -

amount of chloride is not considered as part of the moderating amount of chloride referred to herein as originally deposited on the support.

5 Generally, the carrier is contacted with a silver salt, a silver compound, or a silver complex which has been dissolved in an aqueous solution, so that the carrier is impregnated with said aqueous solution; thereafter the impregnated carrier is separated from the aqueous solution, e.g., by centrifugation or filtration and then dried. The thus obtained impregnated carrier is heated to  
10 reduce the silver to metallic silver. It is conveniently heated to a temperature in the range of from 50°C to 600°C, during a period sufficient to cause reduction of the silver salt, compound or complex to metallic silver and to form a layer of finely divided silver, which is bound to the surface of the carrier, both the  
15 exterior and pore surface. Air, or other oxidizing gas, reducing gas, an inert gas or mixtures thereof may be conducted over the carrier during this heating step.

There are several known methods to add the silver to the carrier or support. The carrier may be impregnated with an aqueous  
20 solution containing silver nitrate dissolved therein, and then dried, after which drying step the silver nitrate is reduced with hydrogen or hydrazine. The carrier may also be impregnated with an ammoniacal solution of silver oxalate or silver carbonate, and then dried, after which drying step the silver oxalate or silver  
25 carbonate is reduced to metallic silver by heating, e.g., to 600°C. Specific solutions of silver salts with solubilizing and reducing agents may be employed as well, e.g., combinations of the vicinal alkanolamines, alkyldiamines and ammonia. One such example of a solution of silver salts comprises an impregnating solution  
30 comprising a silver salt of a carboxylic acid, an organic amine alkaline solubilizing/reducing agent, and an aqueous solvent.

These solubilizing/reducing agents are generally added in the amount of from about 0.1 to about 10 moles per mole of silver present.

- 13 -

One method of preparing the silver containing catalyst can be found in U.S. Patent 3,702,259. Other methods for preparing the silver-containing catalysts which in addition contain higher alkali metal promoters can be found in U.S. Patent 4,010,115; and U.S. Patent 4,356,312; U.S. Patent 3,962,136 and U.S. Patent 4,012,425, 1977. Methods for preparing silver-containing catalysts containing higher alkali metal and rhenium promoters can be found in U.S. Patent No. 4,761,394, and methods for silver-containing catalysts containing higher alkali metal and rhenium promoters and rhenium co-promoters can be found in U.S. Patent No. 4,766,105. Methods for preparing silver-containing catalysts with a variety of different promoters are found in U.S. patents 4,908,343 and 5,057,481.

The concentration of the silver (expressed as the metal) in the silver-containing solution will range from 1 g/l up to the solubility limit when a single impregnation is utilized. The concentration of the alkali metal (expressed as the metal) will range from  $1 \times 10^{-3}$  g/l up to 12 g/l and preferably, from  $10 \times 10^3$  g/l to 12 g/l when a single impregnation step is utilized. The concentration of the chloride will range from  $1 \times 10^{-4}$  g/l up to 1 g/l and preferably, from  $5 \times 10^{-4}$  g/l to 0.1 g/l when a single impregnation step is utilized. Concentrations selected within the above noted ranges will depend upon the pore volume of the catalyst, the final amount desired in the final catalyst and whether the impregnation is single or multiple.

The silver catalysts according to the present invention have been shown to have unique start-up characteristics in an ethylene oxidation process. The conditions for carrying out such an oxidation reaction in the presence of the silver catalysts according to the present invention broadly comprise those already described in the prior art. This applies, for example, to suitable temperatures, pressures, residence times, diluent materials such as nitrogen, carbon dioxide, steam, argon, methane or other saturated hydrocarbons, to the presence of moderating agents to control the catalytic action, for example, 1-2-dichloroethane, vinyl chloride,

- 14 -

ethyl chloride or chlorinated polyphenyl compounds, to the desirability of employing recycle operations or applying successive conversions in different reactors to increase the yields of ethylene oxide, and to any other special conditions which may be selected in processes for preparing ethylene oxide. Pressures in the range of from atmospheric to about 3500 kPa are generally employed. Higher pressures, however, are not excluded. Molecular oxygen employed as reactant can be obtained from conventional sources. The suitable oxygen charge may consist essentially or relatively pure oxygen, a concentrated oxygen stream comprising oxygen in major amount with lesser amounts of one or more diluents, such as nitrogen and argon, or another oxygen-containing stream, such as air. It is therefore evident that the use of the present silver catalysts in ethylene oxide reactions is in no way limited to the use of specific conditions among those which are known to be effective. For purposes of illustration only, the following table shows the range of conditions that are often used in current commercial ethylene oxide reactor units.



- 15 -

TABLE II

*GHSV	1500-10,000
Inlet Pressure	150-400 psig
<u>Inlet Feed</u>	
Ethylene	1-40%
O <sub>2</sub>	3-12%
Ethane	0-3%
Chlorohydrocarbon moderator	0.3-50 ppmv total
Argon and/or methane and/or nitrogen diluent	Balance
Coolant temperature	180-315 °C
Catalyst temperature	180-325 °C
O <sub>2</sub> conversion level	10-60%
EO Production (Work Rate)	32-320 kg EO/m <sup>3</sup> catalyst/hr.

\*Volume units of gas at standard temperature and pressure passing over one volume unit of packed catalyst per hour.

In general terms an ethylene oxide reactor containing fresh or unused catalyst is started up by first heating the reactor to about 5°C- 50°C below the normal reaction temperature and passing nitrogen over the catalyst. The high temperature converts a significant  
5 portion of the organic nitrogen compounds used in the manufacture of the catalyst to nitrogen-containing gases which are swept up in the nitrogen stream and removed from the reactor. The nitrogen purge may be omitted if the impurities on the catalyst are low. The  
10 nitrogen flow; if utilized, is passed over the catalyst at a flow rate typically between 5 to 40%, preferably between 15 and 25% of the design flow rate. The nitrogen flow may be initiated before reactor heatup, during reactor heatup or after the reactor has reached the desired temperature. The nitrogen gas is typically  
15 passed over the catalyst for a period of time ranging from 1/2 of a day to 7 days. During this purge time the nitrogen stream is

- 16 -

monitored for nitrogen-containing decomposition products from the catalyst. When nitrogen is not used, the reactor may be pressurized with ethylene, methane or other non-oxidizing gas.

After the nitrogen-containing decomposition products have been removed to a suitable low level, generally less than 10 ppm, the recycle loop to the ethylene oxide reactor is then pressurized with ethylene and a suitable ballast gas such as methane in preparation for a start-up. A gas flow rate of between 5 to 40% of design rate, preferably from 15 to 25% of design rate is maintained over the reactor.

C<sub>2</sub>H<sub>4</sub>

A chlorohydrocarbon moderator is then added to the recycle gas stream being fed to the ethylene oxide reactor. The amount of chlorohydrocarbon moderator is added slowly over a period of several hours until its concentration in the loop is from 0.3 ppmv to 25 ppmv. Suitable chlorohydrocarbons used as moderators comprise the C<sub>1</sub> to C<sub>8</sub> chlorohydrocarbons, preferably C<sub>1</sub> to C<sub>4</sub> hydrocarbons and most preferably C<sub>1</sub> to C<sub>2</sub> chlorohydrocarbons. Preferred moderators are ethyl chloride, ethylene dichloride and vinyl chloride, particularly ethyl chloride.

C<sub>2</sub>H<sub>5</sub>Cl

After the chlorohydrocarbon moderator has reached the desired level, oxygen is then added to the recycle feed stream at initially from 5 to 40% of design rate, preferably from 15 to 25% of design rate. Reaction initiation will occur within a few minutes after the addition of the oxygen, after which point the oxygen feed to the reactor, the feed gas to the reactor and the reactor temperature are raised to approximately the design conditions over a period of time ranging from about 15 minutes to about 6 hours.

O<sub>2</sub>

The catalysts of the instant invention provide for an improved start-up procedure for an ethylene oxide reactor whereby their use allows the reactor to be brought onstream at a higher selectivity to ethylene oxide in a shorter period of time than would be the case if conventional catalysts were used.

The invention will be illustrated by the following illustrative embodiments.

- 17 -

Illustrative EmbodimentsIllustrative Embodiment 1

The following illustrative embodiment describes typical preparative techniques for making the catalysts of the instant invention (and comparative catalysts) and the typical technique for measuring the properties of these catalysts.

Part A: Preparation of stock silver oxalate/ethylene-diamine solution for use in catalyst preparation:

- 1) Dissolve 415 grams (g) of reagent-grade sodium hydroxide in 2340 millilitres (ml) deionized water. Adjust the temperature to 50 °C.
- 2) Dissolve 1699 g of "KD" (high purity) silver nitrate in 2100 ml deionized water. Adjust the temperature to 50°C.
- 3) Add sodium hydroxide solution slowly to silver nitrate solution with stirring while maintaining a temperature of 50°C. Stir for 15 minutes after addition is complete, and then lower the temperature to 40°C.
- 4) Insert clean filter wands and withdraw as much water as possible from the precipitate created in step (3) in order to remove sodium and nitrate ions. Measure the conductivity of the water removed and add back as much fresh deionized water as was removed by the filter wands. Stir for 15 minutes at 40°C. Repeat this process until the conductivity of the water removed is less than 90 µmho/cm. Then add back 1500 ml deionized water.
- 5) Add 630 g of high-purity oxalic acid dihydrate in approximately 100 g increments. Keep the temperature at 40°C and stir to mix thoroughly. Add the last portion of oxalic acid dihydrate slowly and monitor pH to ensure that pH does not drop below 7.8.
- 6) Remove as much water from the mixture as possible using clean filter wands in order to form a highly concentrated silver-containing slurry. Cool the silver oxalate slurry to 30°C.
- 7) Add 699 g of 92 percent weight (%w) ethylenediamine (8% deionized water). Do not allow the temperature to exceed 30°C during addition.

- 18 -

The above procedure yields a solution containing approximately 27-33%w silver which provides the "stock solution" used in the preparation of Catalysts A through E below.

Part B: Preparation of impregnation solutions

5        For Comparative Catalyst A

129.7 Grams of silver stock solution containing 29.7% Ag was diluted with 14 grams of water and 6.3 grams of monoethanolamine. 0.0285 Grams of  $\text{NH}_4\text{F}$  was dissolved in 2 ml of water and added to the silver solution. CsOH (50% solution in water) in an amount of 0.0582 grams was added to 50 grams of the above diluted silver solution and the resulting mixture was used for the carrier impregnation.

Ag / Cs / silver  
and Cl.

For Catalyst B

151.7 Grams of stock silver solution containing 30.28% Ag was diluted with 7.5 grams of monoethanolamine and 19.8 grams of water. 0.036 Grams of  $\text{NH}_4\text{F}$  and 0.0254 grams of  $\text{NH}_4\text{Cl}$  were dissolved in 2 ml of water and added to the diluted silver solution. A white precipitate of AgCl resulted upon addition, which dissolved upon further stirring. CsOH (50% solution in water) in an amount of 0.0693 grams was added to the above solution and the resulting mixture was used for the carrier impregnation.

For Catalyst C

151.9 Grams of stock silver solution containing 34.2% Ag was diluted with 27 grams of 50/50 (v/v) mixture of monoethanolamine/ $\text{H}_2\text{O}$ . 0.036 Grams  $\text{NH}_4\text{F}$  and 0.025 grams of  $\text{NH}_4\text{Cl}$  were dissolved in 2 ml water and added to the diluted silver solution. CsOH (50% solution in water) in an amount of 0.0592 grams was added to the above solution and the resulting mixture was used for the carrier impregnation.

For Comparative Catalyst D

131.2 Grams of stock silver solution containing 29.77% Ag was diluted with 19.8 grams of 50/50 (v/v) mixture of monoethanolamine/ $\text{H}_2\text{O}$ . 0.104 Grams of NaCl were dissolved in 2 ml of water and the resulting solution was added to the diluted silver solution. A white precipitate of AgCl resulted upon addition, but

- 19 -

redissolved upon stirring. CsOH (50% solution in water) in an amount of 0.048 grams was added to 50 grams of the above solution and the resulting mixture was used for the carrier impregnation.

For Catalyst E

5           151.7 Grams of stock silver solution containing 30.28% Ag was diluted with 7.5 grams of monoethanolamine and 19.8 grams of water. 0.036 Grams of  $\text{NH}_4\text{F}$  and 0.0508 grams  $\text{NH}_4\text{Cl}$  were dissolved in 2 ml water and added to the above diluted silver solution. CsOH (50% solution in water) in an amount of 0.0766 grams was added to 60  
10 grams of the above solution and the resulting mixture was used for the carrier impregnation.

Part C: Catalyst impregnation and curing

Catalyst carrier D which is described in Table 1 is a preferred support for the instant invention and is used in the following  
15 examples and illustrative embodiments unless otherwise stated.

Approximately 30 g of carrier C are placed under 25 mm vacuum for 3 minutes at room temperature. Approximately 50 g of doped impregnating solution is then introduced to submerge the carrier, and the vacuum is maintained at 25 mm for an additional 3 minutes.  
20 At the end of this time, the vacuum is released, and excess impregnating solution is removed from the carrier by centrifugation for 2 minutes at 500 rpm. If the impregnating solution is prepared without monoethanolamine, then the impregnated carrier is then cured by being continuously shaken in a 8500 litre/hr. air stream flowing  
25 across a cross-sectional area of approximately 3-5 square inches at 250-270°C for 5-6 minutes. If significant monoethanolamine is present in the impregnating solution, then the impregnated carrier is cured by being continuously shaken in a 8500 litre/hr. air stream at 250°C for 2.5 minutes, followed by a 2800 litre/hr. air stream at  
30 270°C for 7.5 minutes (all over a cross-section area of approximately 19.3-32.2  $\text{cm}^2$ ). The cured catalyst is then ready for testing.

This procedure will yield catalysts A through E with the properties show in Table III below.

- 20 -

Catalyst F was prepared using a double impregnation technique. In this technique 120 g of carrier was impregnated with 240 g of silver stock solution with a specific gravity of 1.555. The impregnated carrier was dried/roasted to decompose silver salts to metallic silver. Water pore volume was determined after the first impregnation and was used to calculate the dopant concentrations. 164.7 Grams of stock silver solution with a specific gravity of 1.55 was diluted with 13.9 g of monoethanolamine. 0.1722 Grams of ammonium chloride and 0.0408 g of ammonium fluoride were dissolved in 2.5 g of water and added to the silver solution. 0.0742 Grams of cesium hydroxide (50% solution in water) were added to 60 g of the above silver solution and the resulting mixture was used for the second impregnation of the carrier. The catalyst was cured in a manner similar to that described above. The composition of the resulting catalyst is shown in Table III below.

TABLE III

<u>CATALYST</u>	<u>Ag, wt%</u>	<u>Cs, ppm</u>	<u>Cl, ppm</u>	<u>Cl/Ag Mole</u> <u>Ratio,</u>	
A	14.5	285	0	0	<i>Comp</i>
B	15.6	273	53	$1.03 \times 10^{-3}$	<i>Inv.</i>
C	15.4	283	53	$1.05 \times 10^{-3}$	
D	14.5	257	238	$4.99 \times 10^{-3}$	<i>Comp</i>
E	14.6	306	106	$2.21 \times 10^{-3}$	<i>Inv.</i>
F	27.5	260	260	$2.88 \times 10^{-3}$	

The actual silver content of the catalyst can be determined by any of a number of standard, published procedures. The actual level of cesium on the catalyst can be determined by employing a stock cesium hydroxide solution, which has been labelled with a radioactive isotope of cesium, in catalyst preparation. The cesium content of the catalyst can then be determined by measuring the radioactivity of the catalyst. Alternatively, the cesium content of the catalyst can be determined by leaching the catalyst with boiling

- 21 -

deionized water. In this extraction process cesium, as well as other alkali metals, is measured by extraction from the catalyst by boiling 10 grams of whole catalyst in 20 millilitres of water for 5 minutes, repeating the above two more times, combining the above  
5 extractions and determining the amount of alkali metal present by comparison to standard solutions of reference alkali metals using atomic absorption spectroscopy (using Varian Techtron Model 1200 or equivalent). The actual level of chloride on the catalyst was determined by calculation from the amounts impregnated in the  
10 catalyst. The chloride content can also be determined by known analytical techniques such as by fluorescent X-ray analysis.

#### Part D: Standard Microreactor Catalyst Test

##### Conditions/Procedure

3 to 5 Grams of crushed catalyst of 1.410-0.841 mm (14-20 mesh)  
15 are loaded into a 6.4 mm diameter stainless steel U-shaped tube. The U tube is immersed in a molten metal bath (heat medium) and the ends are connected to a gas flow system. The weight of the catalyst used and the inlet gas flow rate are adjusted to achieve a gas hourly space velocity of 3300 ml of gas per ml of catalyst per hour.  
20 The inlet gas pressure is 1550 kPa

The gas mixture passed through the catalyst bed (in once-through operation) during the entire test run (including start-up) consists of 30% ethylene, 8.5% oxygen, 5% carbon dioxide, 5 ppmv ethyl chloride with the balance being nitrogen/argon.

25 The start-up procedure involved ramping the temperature from 180°C to 230°C in the following fashion: 1 hour at 180°C, 1 hour at 190°C, 1 hour at 200°C, 1 hour at 210°C, 1 hour at 220°C, 2 hours at 220°C, 2 hours at 225°C, 2 hours at 230°C, and then the temperature was adjusted to provide an oxygen conversion of 40%. Oxygen  
30 conversion (mole %) and selectivity of ethylene to ethylene oxide (mole%) were measured during and after start-up.

Selectivities and oxygen conversions as a function of time are shown in Figures 1 and 2 for Comparative Catalyst A (no chloride) and chloride-containing Catalysts B and C of this invention and in

- 22 -

Figures 3 and 4 for Comparative Catalyst A (no chloride) and Catalyst E of this invention. As can be seen from Figures 1 and 3, the selectivity approaches the final value from the high side for Catalysts B, C and E and from the low side for the Comparative Catalyst A, providing for an earlier enhanced yield of ethylene oxide with the use of the chloride-containing catalysts. From Figures 2 and 4 it can be seen that the Comparative Catalyst A shows a very high oxygen conversion approaching 70%, which provides for a very "hot" start-up which is much more difficult to control than the start-up using the catalysts of this invention.

For Comparative Catalyst D it was found that after start-up the catalyst had suffered a significant selectivity loss (decrease of 3.4%) and activity loss (increase of 35°C) when compared to a catalyst without chloride (Comparative Catalyst A). Catalyst F did not show any loss in selectivity or activity.



C L A I M S

1. A catalyst for the vapour phase production of ethylene oxide from ethylene and oxygen in the presence of a chlorohydrocarbon moderator comprising, prior to the first use of the catalyst, a catalytically effective amount of silver, a promoting amount of  
5 alkali metal, and from  $0.4 \times 10^{-3}$  to  $4 \times 10^{-3}$  moles of chloride per mole of silver deposited on a carrier comprising at least 85 percent by weight of alpha alumina.
2. The catalyst of claim 1 wherein the carrier has a water pore volume between 0.1 and 0.6 ml/g and a surface area between 0.1 and  
10  $3 \text{ m}^2/\text{g}$ .
3. The catalyst of claim 1 wherein the amount of silver is in the range of from 1 to 40 percent by weight of the total catalyst and the amount of alkali metal promoter is in the range of from 10 to  
15 3000 parts per million, expressed as the metal by weight of the total catalyst.
4. The catalyst of claim 3 wherein the silver ranges from 12 to 18 weight percent of the total catalyst and the chloride content ranges from 20 to 200 parts per million by weight of the total catalyst.
5. The catalyst of claim 1 wherein said alkali metal promoter is  
20 selected from potassium, rubidium, cesium, lithium and mixtures thereof.
6. The catalyst of claim 1 wherein one or more additional promoters or copromoters are present, selected from rhenium, sulphur, molybdenum, tungsten and chromium.
7. A process for preparing a catalyst for the vapour phase  
25 production of ethylene oxide from ethylene and molecular oxygen which comprises impregnating a carrier comprising at least 85 percent by weight of alpha alumina with one or more solutions comprising solvent having silver compound(s) dissolved therein,  
30 alkali metal compound(s) dissolved therein and chloride-containing

- 24 -

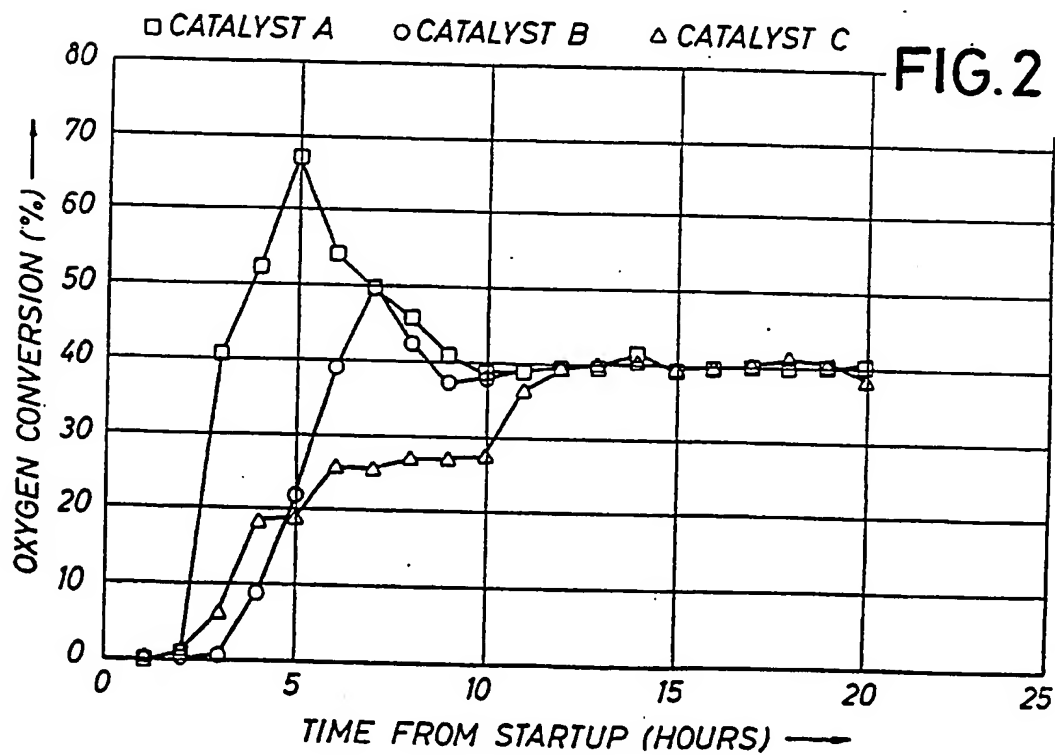
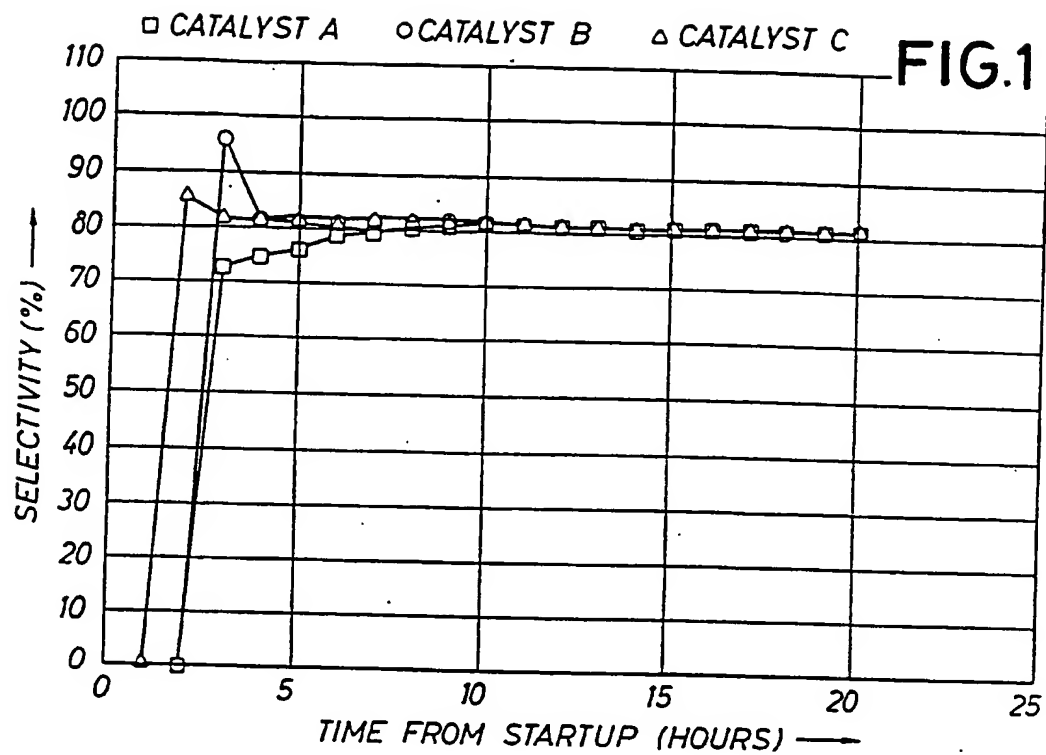
compounds dissolved therein sufficient to deposit on the support from 1 to 40 percent by weight of the total catalyst of the silver compound(s), expressed as the metal, from 10 to 3000 parts per million by weight of alkali metal compound(s), expressed as the metal, by weight of the total catalyst and from  $0.4 \times 10^{-3}$  to  $4 \times 10^{-3}$  moles of chloride per mole of silver deposited.

8. The process of claim 7 wherein after impregnation, the silver is reduced to metallic silver by heating at a temperature between  $50^{\circ}\text{C}$  to  $600^{\circ}\text{C}$ .

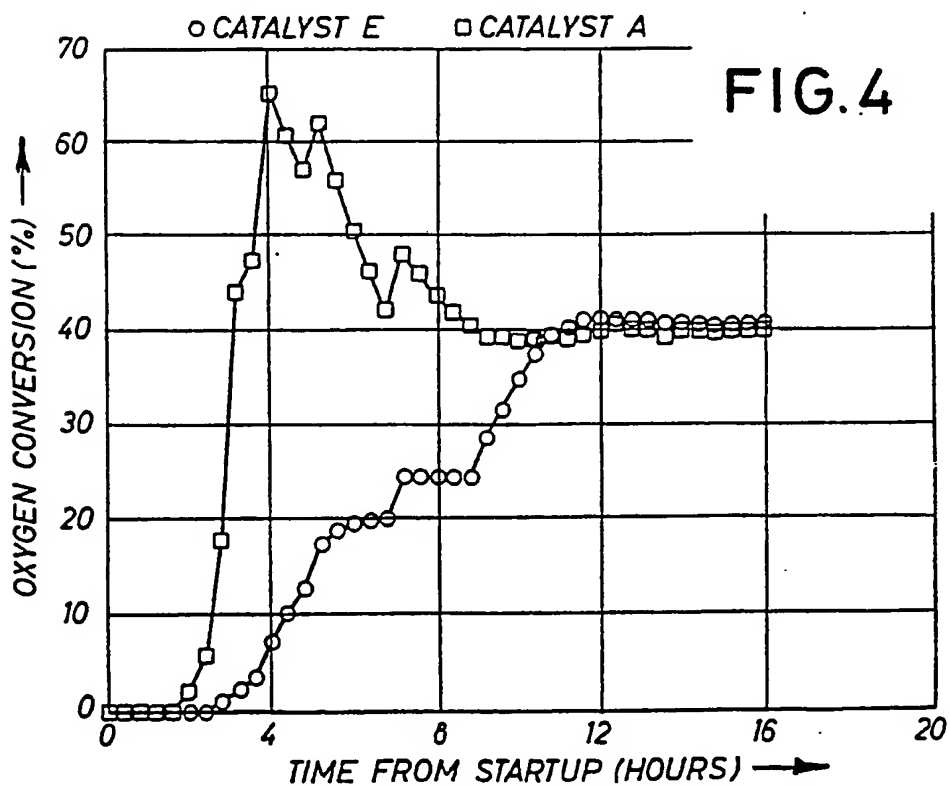
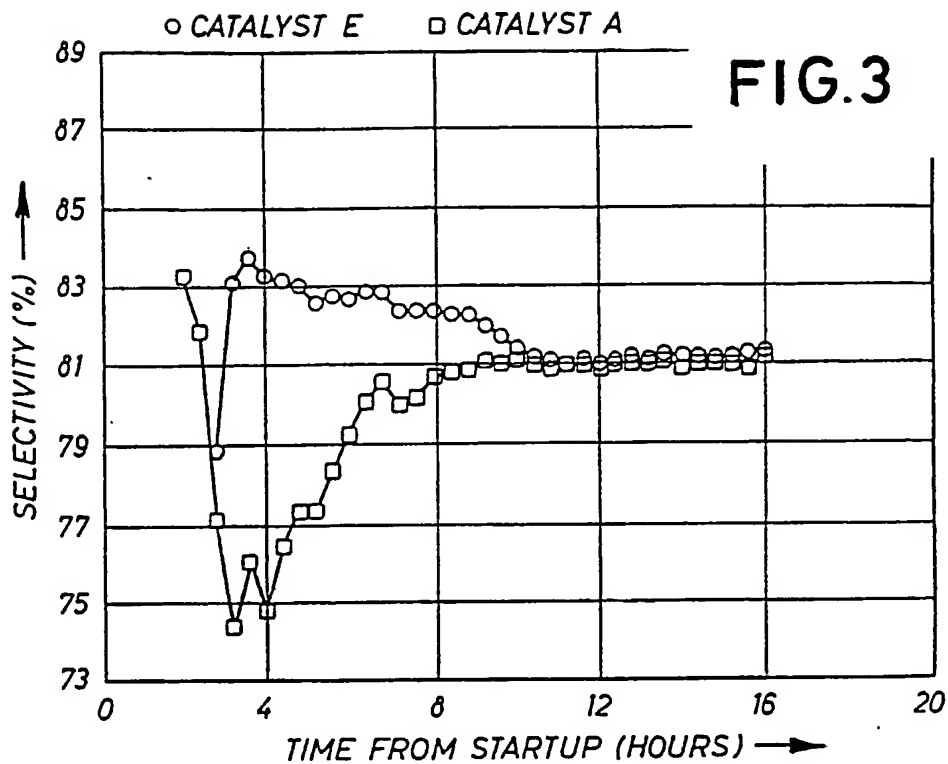
9. The process of claim 7 or 8 wherein the chloride-containing compound is an alkali metal chloride or ammonium chloride.

10. In the process of starting up an ethylene oxide reactor containing fresh catalyst by heating the catalyst to ethylene oxide forming temperatures in the presence of ethylene, oxygen and a chlorohydrocarbon moderator, the improvement which comprises using as the fresh catalyst, a catalyst comprising a catalytically effective amount of silver, a promoting amount of alkali metal, and from  $0.4 \times 10^{-3}$  to  $4 \times 10^{-3}$  moles of chloride per mole of silver, deposited on a carrier comprising at least 85 percent by weight of alpha alumina.

1/2



2/2



## INTERNATIONAL SEARCH REPORT

Int. Application No

PCT/EP 94/02783

A. CLASSIFICATION OF SUBJECT MATTER  
 IPC 6 B01J23/66 C07D301/10

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 B01J C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 059 422 (MITSUBISHI PETROCHEMICAL CO., LTD.) 8 September 1982 cited in the application see the whole document ---	1
A	EP,A,0 172 565 (MITSUBISHI PETROCHEMICAL CO., LTD.) 26 February 1986 see the whole document ---	1
A	EP,A,0 247 414 (MITSUBISHI PETROCHEMICAL CO., LTD) 2 December 1986 see the whole document ---	1
-/--		

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

30 November 1994

Date of mailing of the international search report

13.12.94

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
 NL - 2280 HV Rijswijk  
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
 Fax (+31-70) 340-3016

Authorized officer

Devisme, F

## INTERNATIONAL SEARCH REPORT

Int. l. Application No

PCT/EP 94/02783

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Week 8329, Derwent Publications Ltd., London, GB; AN 83-714123 & JP,A,58 098 144 (MITSUBISCHI PETROCHEMICAL KK) 10 June 1983 see abstract ---	1
A	DATABASE WPI Week 9230, Derwent Publications Ltd., London, GB; AN 92-248428 & SU,A,1 685 510 (V. A. DAVYDOV ET AL.) 23 October 1991 see abstract ---	1
A	US,A,4 908 343 (MADAN M. BHASIN) 13 March 1990 -----	

# INTERNATIONAL SEARCH REPORT

Information on patent family members

Int. Application No

PCT/EP 94/02783

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0059422	08-09-82	JP-C- 1620667	09-10-91
		JP-B- 2040378	11-09-90
		JP-A- 57140654	31-08-82
		JP-C- 1643305	28-02-92
		JP-B- 2040375	11-09-90
		JP-A- 57180434	06-11-82
		US-A- 4415476	15-11-83
		US-A- 4414135	08-11-83
EP-A-0172565	26-02-86	JP-A- 61054242	18-03-86
		JP-B- 5029501	30-04-93
		JP-A- 61071837	12-04-86
		JP-B- 5016903	05-03-93
		JP-A- 61103545	22-05-86
		US-A- 4786624	22-11-88
		US-A- 4690913	01-09-87
EP-A-0247414	02-12-87	CA-A- 1300586	12-05-92
		DE-A- 3773995	28-11-91
		JP-A- 63116743	21-05-88
		US-A- 4812437	14-03-89
US-A-4908343	13-03-90	US-A- 5057481	15-10-91

**THIS PAGE BLANK (USPTO)**



**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**

**THIS PAGE BLANK (USPTO)**